

**The effect of local  
biogenic emissions**

R. Seco et al.

# Contrasting winter and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: the effect of local biogenic emissions

R. Seco<sup>1</sup>, J. Peñuelas<sup>1</sup>, I. Filella<sup>1</sup>, J. Llusà<sup>1</sup>, R. Molowny-Horas<sup>2</sup>, S. Schallhart<sup>3</sup>, A. Metzger<sup>4</sup>, M. Müller<sup>3</sup>, and A. Hansel<sup>3</sup>

<sup>1</sup>Unitat d'Ecologia Global CREAM-CEAB-CSIC, Centre de Recerca Ecològica i Aplicacions Forestals (CREAF), Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Catalunya, Spain

<sup>2</sup>Centre de Recerca Ecològica i Aplicacions Forestals (CREAF), Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Catalunya, Spain

<sup>3</sup>Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstrasse 25, 6020 Innsbruck, Austria

<sup>4</sup>Ionicon Analytik, Eduard-Bodemgasse 3, 6020 Innsbruck, Austria

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Received: 17 May 2011 – Accepted: 11 July 2011 – Published: 19 July 2011

Correspondence to: R. Seco (roger@creaf.uab.cat)

Published by Copernicus Publications on behalf of the European Geosciences Union.

---

**The effect of local biogenic emissions**

R. Seco et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Atmospheric volatile organic compounds (VOCs) are involved in ozone and aerosol generation, thus having implications for air quality and climate. VOCs and their emissions by vegetation also have important ecological roles as they can protect plants from stresses and act as communication cues between plants and between plants and animals. In spite of these key environmental and biological roles, the reports on seasonal and daily VOC mixing ratios in the literature for Mediterranean natural environments are scarce.

We conducted seasonal (winter and summer) measurements of VOC mixing ratios in an elevated (720 m a.s.l.) holm oak Mediterranean forest site near the metropolitan area of Barcelona (NE Iberian peninsula). Methanol was the most abundant compound among all the VOCs measured in both seasons. While aromatic VOCs showed almost no seasonal variability, short-chain oxygenated VOCs presented higher mixing ratios in summer, presumably due to greater emission by vegetation and increased photochemistry, both enhanced by the high temperatures and solar radiation in summer. Isoprenoid VOCs showed the biggest seasonal change in mixing ratios: they increased by one order of magnitude in summer, as a result of the vegetation's greater physiological activity and emission rates. The maximum diurnal concentrations of ozone increased in summer too, most likely due to more intense photochemical activity and the higher levels of VOCs in the air.

The daily variation of VOC mixing ratios was mainly governed by the wind regime of the mountain, as the majority of the VOC species analyzed followed a very similar diel cycle. Mountain and sea breezes that develop after sunrise advect polluted air masses to the mountain. These polluted air masses had previously passed over the urban and industrial areas surrounding the Barcelona metropolitan area, where they were enriched in  $\text{NO}_x$  and in VOCs of biotic and abiotic origin. Moreover, these polluted air masses receive additional biogenic VOCs emitted in the local valley by the vegetation, thus enhancing  $\text{O}_3$  formation in this forested site. The only VOC species that showed

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



a somewhat different daily pattern were monoterpenes because of their local biogenic emission. Isoprene also followed in part the daily pattern of monoterpenes, but only in summer when its biotic sources were stronger. The increase by one order of magnitude in the concentrations of these volatile isoprenoids highlights the importance of local biogenic summer emissions in these Mediterranean forested areas which also receive polluted air masses from nearby or distant anthropic sources.

## 1 Introduction

Volatile organic compounds (VOCs) present in the atmosphere have both natural and anthropogenic sources. Among the natural origins, emission by vegetation is regarded as the greatest source at a global scale (Guenther et al., 2006). VOCs play several key roles in atmospheric chemistry which make them highly relevant for study, for example their implication in tropospheric ozone and aerosol generation. VOCs, together with nitrogen oxides ( $\text{NO}_x$ ) and solar radiation are the ingredients needed to promote the photochemical formation of tropospheric ozone (Atkinson, 2000; Sillman, 1999). Ozone is an oxidant pollutant that has negative effects on plants (Fowler et al., 2009), poses a threat to human health (Lippmann, 1993) and acts in the troposphere as a greenhouse gas. VOCs are also precursors of atmospheric aerosols (Kavouras et al., 1998; Tunved et al., 2006), which can have significant climate implications (Kulmala et al., 2004; Pacifico et al., 2009). In a context of global change, the relationships between VOCs, particles and ozone are a hot topic in current scientific research (Peñuelas and Staudt, 2010). They all are involved in biogeochemical cycles and take part with other global change drivers in complex feedbacks with the climate (Arneeth et al., 2010). Atmospheric VOCs and their emissions by vegetation are also ecologically important because VOCs can protect plants against high temperatures (Peñuelas et al., 2005; Singaas and Sharkey, 1998), high irradiance (Peñuelas and Munné-Bosch, 2005), and oxidative stress (Peñuelas and Llusià, 2002; Velikova et al., 2005). In addition, they also act as plant-plant communication signals (Baldwin et al., 2006; Heil and

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The effect of local biogenic emissions**

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Kost, 2006; Kegge and Pierik, 2010; Peñuelas et al., 1995; Pierik et al., 2003; Seco et al., 2011). Likewise, VOCs play a role in plant-animal relationships, not only involving plant-pollinator relationships (Wright and Schiestl, 2009) or direct defense against herbivores, but also indirect defense through the attraction of the natural enemies of the herbivores (Kessler and Baldwin, 2001; Llusà and Peñuelas, 2001; Pichersky and Gershenson, 2002).

In the Mediterranean area, where the potential for biogenic VOC emissions and photochemistry is high, ozone and particle formation can be elevated and the ecological role of VOCs can be very significant. However, there is scarce information on tropospheric VOC mixing ratios in the Mediterranean region. Ozone has been measured in high concentrations in the Mediterranean area (Gimeno et al., 1995; Ribas and Peñuelas, 2004; Ziomias, 1998), and has already been reported to produce damage to plants in the Western Mediterranean Basin (Ribas et al., 2005; Sanz et al., 2000). Moreover, ozone concentrations have been found to increase with altitude (Diaz-de-Quijano et al., 2009; Evtuygina et al., 2009; Ribas and Peñuelas, 2006).

In recent years, the proton transfer reaction mass spectrometer (PTR-MS) has enabled the simultaneous measuring of several VOCs, including some oxygenated VOCs that are difficult to measure with other techniques (Seco et al., 2007, 2008). Also, PTR-MS has improved the temporal resolution of these measurements, to the point of making the use of micrometeorological techniques possible (Karl et al., 2001). Of late, papers have reported several concomitant surface-level VOC mixing ratios in natural areas, taking advantage of the PTR-MS technology in boreal and temperate regions (Holst et al., 2010; Jordan et al., 2009; Lappalainen et al., 2009; Ruuskanen et al., 2009; e.g. Spirig et al., 2005). Nevertheless, there are few studies dealing with Mediterranean ecosystems (Davison et al., 2009).

In this paper we report VOC data gathered during 2009 in an elevated site highly representative of the montane Mediterranean forest (Terradas, 1999), located in a forested mountain slope, in the Western Mediterranean Basin. We compared the VOC mixing ratios between winter (February–March) and summer (July–August), and analysed

their relationship with meteorological data, and with ozone (O<sub>3</sub>) and nitrogen oxides (NO<sub>x</sub>, i.e. NO and NO<sub>2</sub>) concentrations. We also compared the VOC mixing ratio values and daily trends at this Montseny (MSY) site with those reported in the existing literature for other natural areas worldwide.

## 2 Methods

### 2.1 Measurement site

The Montseny site (MSY) was located within a densely forested natural park about 60 km to the NNE of the city of Barcelona (Catalonia, NE of the Iberian peninsula) and 25 km from the Mediterranean coast (41°46'45.63" N 02°21'28.92" E, 720 m a.s.l.; Fig. 1). The site is highly representative of the montane holm oak (*Quercus ilex* L.) forests in the Mediterranean regions of France, Italy, Greece and eastern Spain (Terradas, 1999). At Montseny, these are dense forests of resprout origin, which evolved from coppicing until the 1950s and selection thinning afterwards (Avila and Rodrigo, 2004).

To our knowledge, this was the first time that VOC mixing ratios were measured continuously over several days at this Mediterranean forest location, which has a long record of other ecological and biogeochemical parameters such as nutrient cycling (Avila et al., 2002), dry and wet deposition (Avila et al., 1998, 2007, 2010; Avila and Rodà 2002; Avila and Alarcon 2003), hydrology (Piñol et al., 1992), and particulate matter (Perez et al., 2008; Pey et al., 2009), among others.

### 2.2 VOC measurements

VOC measurements were conducted with two different Proton Transfer Reaction-Mass Spectrometers (PTR-MS), one for each season, installed in an uninhabited traditional rural house (La Castanya). The house is situated in a forest clearing in a south-facing

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



slope of the mountain, surrounded by the holm oak forest. Both PTR–MS set-ups sampled ambient air through a heated inlet line (4 m long), made either of deactivated Sulfinert (winter) or teflon (summer) tube, installed at 3 m height in a forest gap. The inlet line was filtered with a teflon membrane (winter) or glass wool (summer) to prevent dust and particle intake. System background for both instruments was measured approximately every two hours by sampling zero air made by passing air through a catalytic converter, and instrument sensitivities were obtained by frequent calibrations with gas standards (Table 1).

For VOC monitoring during the winter measurements, a newly developed Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS) was deployed. It combined a Time-of-Flight MS detector (Tofwerk AG, Switzerland) with the characteristic chemical ionization system that defines PTR systems. A thorough description and characterization of the PTR-TOF instrument is given by Graus et al. (2010). The PTR-ToF-MS drift tube was operated at 2.3 mbar, 600 V, and 50 °C which corresponds to a  $E/N$  ratio of 130 Td ( $E$  being the electric field strength and  $N$  the gas number density; 1 Td =  $10^{-17}$  V cm<sup>2</sup>). Sensitivity calibrations for the PTR-TOF were performed by dynamic dilution of VOCs using a multi-component gas standard (Apel Riemer Environmental Inc., USA). The calibration gas contained acetone, acetonitrile, acrolein, benzene, 2-butanone, ethanol, formaldehyde, hexanone, isoprene, methanol, monoterpenes ( $\alpha$ -pinene), toluene, o- and p-xylene. The time-of-flight path length is sensitive to temperature variation and therefore mass scale calibration was done continuously by adding dichlorobenzene (protonated  $m/z = 146.9763$ ) and trichlorobenzene (protonated  $m/z = 180.9373$ ) to the PTR-TOF inlet.

During the summer measurements, the site was equipped with a High Sensitivity Proton Transfer Reaction-Quadrupole-Mass Spectrometer (PTR-Quad-MS, described by Lindinger et al., 1998). This instrument was operated at 2.3 mbar, 580 V, and 50 °C drift tube conditions, which corresponds to a  $E/N$  of 122 Td. Sensitivity calibrations for the PTR-Quad-MS were performed by dynamic dilution of an aromatic VOC gas standard (TO-14A, Restek, Bellefonte, PA, USA). The calibration gas contained benzene,

**The effect of local biogenic emissions**

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

toluene, chlorobenzene, dichlorobenzene, styrene, ethyl benzene, xylene, trimethylbenzene, and trichlorobenzene. In addition, vapors of isoprene and monoterpene ( $\alpha$ -pinene and limonene) liquid standards were sampled to measure their relative transmission efficiency and their fragmentation pattern. Mixing ratios of VOCs not present in the calibration standard were calculated taking into account the VOC relative transmission, their measured fragmentation pattern and their proton transfer reaction rate coefficients reported elsewhere (Zhao and Zhang, 2004) as described by de Gouw and Warneke (2007).

These PTR systems have differences in the mass resolution of the VOCs analyzed, since the ToF MS is capable of separating isobaric compounds that the PTR-Quad-MS detects at one single mass. Such differences are shown in Table 1, where the masses measured and the VOC assigned to each mass are displayed. In the case of the ToF, isobaric VOCs can be distinguished according to their exact mass, while in the case of the Quadrupole the identification of VOCs is liable to interferences, although identification was based on calibrations, experience, and well-known and almost interference-free VOC-mass correspondences (de Gouw and Warneke, 2007). For example, we report measurements of protonated mass 47 in summer and attribute them to formic acid/ethanol (Table 1), because the PTR-Quad-MS is not able to separate these two compounds. In the winter measurements, the PTR-ToF-MS could have identified each of them separately, but only ethanol was detected (Table 1). In the case of monoterpenes, neither PTR-MS system could separate the different isomers. Thus, additionally, samples were taken for monoterpene determination via gas chromatography-mass spectrometry (GC-MS). Using a teflon line to sample from the same inlet point as the PTR-MS systems and by means of a pump, ambient air was drawn through a tube (8 cm long and 0.3 cm internal diameter) manually filled with terpene adsorbents Carboxen 1003, and Carboxen Y (Supelco, Bellefonte, PA, USA) separated by plugs of quartz wool. The cartridges were prepared and then analysed in the laboratory as described in Llusia et al. (2010).



**The effect of local biogenic emissions**

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

For clarity, we have divided the measured VOCs into three groups according to their structure and characteristics. One group is composed of short-chain oxygenated compounds (oxVOCs): methanol, acetone, acetaldehyde, acetic acid, and formic acid/ethanol (see Seco et al., 2007 for a review). The second group is formed by the isoprenoids: isoprene and monoterpenes, and we additionally included here the compounds methyl vinyl ketone (MVK) and methacrolein (MACR), which are oxidation products of isoprene. The third group contains the aromatic volatiles: benzene, toluene, and C8-aromatics (a term that includes compounds like xylenes). Finally, we also analyzed acetonitrile.

### 2.3 Meteorology and measurements of inorganic gaseous pollutants

During both periods, meteorological data such as temperature, relative humidity, wind direction and speed, precipitation, and solar radiation was gathered from an air monitoring station that is part of the EUSAAR network (European Supersites for Atmospheric Aerosol Research, recently created to integrate the measurements of atmospheric aerosol properties at 21 high quality European ground-based stations). This station was located 200 m away from the PTR-MS sampling site, in the same slope of the mountain and at the same altitude (720 m a.s.l.). The actual measurements were taken from a tower, at 10 m height (Pandolfi et al., 2011).

Real time measurements of ambient air levels of O<sub>3</sub> and NO<sub>x</sub> (NO and NO<sub>2</sub>) were provided by conventional gas phase air pollution monitors installed at the same station and maintained by the Department of the Environment of the Catalan Government (Generalitat de Catalunya). Levels of NO<sub>x</sub> were measured by a chemiluminescence analyzer (model 42iTL, Thermo Scientific) and those of O<sub>3</sub> by the ultraviolet photometric method (model 48AUV, MCV S.A., Barcelona).

## 2.4 Data analysis and statistics

Calculations of VOC mixing ratios from the PTR-MS data, together with the treatment and graphing of the data time series, were conducted using Igor Pro (Wavemetrics Inc., Portland, OR, USA). The correlation coefficients between all the available data variables (VOC mixing ratios, wind, temperature, solar radiation, and NO<sub>2</sub> and O<sub>3</sub>) were calculated, in order to conduct a preliminary screening of possible relationships (see Supplement). For this purpose the Statistica (StatSoft Inc., Tulsa, USA) package was used. In addition, wavelet analysis was applied to analyze the relationship between VOC mixing ratios and ozone concentrations in summer (see Supplement).

## 3 Results

### 3.1 Meteorological conditions and atmospheric dynamics

The MSY site presents a typical Mediterranean climate with warm summers, temperate winters and irregular precipitation rates (Perez et al., 2008). In fact, precipitation was practically nonexistent during the periods reported in this paper. Average maximum solar radiation reached around 600 W m<sup>-2</sup> in winter and 800 W m<sup>-2</sup> in summer (Fig. 2), and consequently the average temperatures differed 11–15 °C between the two periods (7–13 °C and 19–27 °C daily averages in winter and summer, respectively), while relative humidity showed almost identical daily profiles (Fig. 2).

Air circulation in the MSY site is strongly determined by the topography of the valley, and two main wind directions are usually recorded (Fig. 3). The southerly direction is present when the mountain and sea breezes develop during daytime, entering the valley from the south. This is when the highest wind speeds are usually recorded. The westerly direction corresponds to intense advections from the north and north-west, channeled into the valley with a western direction (as was the case during the period 5–7 March), and to drainage flows during the night (Perez et al., 2008). The highest

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



wind speeds for winter were measured during the Atlantic advection scenario (days 5–7 March) with values of up to  $10 \text{ m s}^{-1}$ . There were some problems encountered with the recording software when measuring the wind speeds for summer and so the magnitudes displayed seem to be lower than the real wind speeds of those days (Fig. 3).

### 3.2 $\text{O}_3$ , $\text{NO}$ and $\text{NO}_2$ concentrations

Ozone concentrations showed similar values during the night and early morning both in winter and summer (average around  $75 \mu\text{g m}^{-3}$ ). About two hours after sunrise they increased up to an average of  $128 \mu\text{g m}^{-3}$  in summer (around 14:00 h GMT) and  $95 \mu\text{g m}^{-3}$  in winter (peaks around 11:00 h and 15:00 h GMT) (Fig. 4).  $\text{NO}_2$  concentrations showed a similar daily profile, with very similar summer and winter values during night and morning (average around  $2 \mu\text{g m}^{-3}$ ), and then an increase (delayed by around 2 h with respect to the rise in  $\text{O}_3$ ) reaching a first peak at 13:00 h and a second peak around 17:00 h (winter) or 19:00 h (summer). Maximum average values were  $11.6 \mu\text{g m}^{-3}$  for winter and  $7.5 \mu\text{g m}^{-3}$  for summer (Fig. 4).  $\text{NO}$  concentrations were usually below the limit of detection ( $<1 \mu\text{g m}^{-3}$ ) of the instrumentation deployed by the government at MSY. Only some episodes reaching peaks of  $2\text{--}6 \mu\text{g m}^{-3}$  in winter were recorded, resulting in maximum winter averages of  $1.6 \mu\text{g m}^{-3}$ , which took place when  $\text{NO}_2$  concentrations also peaked (data not shown).

### 3.3 VOC mixing ratios

#### 3.3.1 Seasonal differences

All the VOC mixing ratios measured during the winter and summer campaigns as well as their mean daily cycles are displayed in Figs. 5, 6, and 7, while Table 2 lists maximum and minimum values of the same data. Almost all the VOCs analyzed showed higher average mixing ratios during the summer period than in winter. Only some aromatic VOCs, normally linked to anthropogenic sources, had lower (benzene) or

## The effect of local biogenic emissions

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

similar (toluene and C8-aromatics) mixing ratios in summer compared to winter (Fig. 7). The greatest difference in mixing ratios between seasons corresponded to the isoprenoids (Fig. 6), as seen by the 10-fold (isoprene and also its degradation products MVK/MACR) and 21-fold (monoterpenes) increases in their hourly average maxima (Table 2). In the case of monoterpenes, GC-MS analysis showed that the most abundant species were the same in winter and summer,  $\alpha$ -pinene being the most abundant one among them (51.4/31.9% in winter/summer), followed by sabinene +  $\beta$ -pinene (27.1/28.8%) and limonene (9.5% in both seasons).

The VOC species with the highest mixing ratios in both winter and summer was methanol (showing peaks of up to 9.7/13.4 ppbv and maximum hourly averages of 2.7/6 ppbv in winter/summer), followed in winter by ethanol (with peaks of 8.9 ppbv and maximum averages of 2 ppbv) and in summer by acetone (reaching up to 5.9 ppbv and maximum averages of 3.8 ppbv, Fig. 5, Table 2). Regarding isoprenoids, monoterpenes were more abundant (reaching maximum averages of 1.4 ppbv) than isoprene (reaching maximum averages of 0.75 ppbv) in summer, whereas in winter both VOCs showed similar mixing ratios (around 0.07 ppbv maximum averages). Among the aromatic VOCs, toluene presented the highest mixing ratios (with peaks below 2 ppbv and maximum averages around 0.4 ppbv) in both seasons (Fig. 7).

### 3.3.2 Average daily cycles

Looking at the daily average mixing ratios and in general terms, all VOCs presented very similar diel cycles with maximum values during the daytime (Fig. 8). Linear correlations between all of them showed variable Pearson's correlation coefficients ( $r$ ), but they were always significant ( $p < 0.01$ ) above 0.31 and with an average of 0.73 in winter and 0.68 in summer (see Table S1 in the Supplement).

When considering the different groups of VOCs separately, it is apparent that although their daily pattern is not exactly the same in summer as in winter all short-chain oxygenated VOCs (oxVOCs) and aromatics have almost the same daily pattern. Relationships between isoprenoid VOCs (isoprene and monoterpenes) showed a mixed

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



behaviour, depending on the season. In winter isoprene showed a diel cycle resembling that of aromatic or oxVOCs (Fig. 8), while in summer its mean daily cycle was not exactly like the any other cycle, neither that of oxVOCs, aromatics nor monoterpenes (Fig. 8).

## 4 Discussion

Our results show almost no seasonal variability for aromatic VOCs, whereas short-chain oxygenated VOCs and isoprenoids in particular presented much higher mixing ratios (one order of magnitude greater) in summer when the vegetation emission rates increased considerably (also by one order of magnitude, Llusia et al., 2011). The highest diurnal concentrations of ozone increased in summer too, probably due to more intense photochemical activity and the higher VOC mixing ratios.

The daily variations in the mixing ratios of most VOCs measured in this study show a very similar pattern. This fact, along with its correspondence in time with the wind direction and speed (Fig. 8), suggests that the changes in VOC mixing ratios are driven by the wind regime of the MSY site, which advects air masses from the metropolitan area of Barcelona during the daytime, and from the north-western pastures and forests during the night.

### 4.1 Seasonal VOC mixing ratios

#### 4.1.1 OxVOCs

Methanol is the second most abundant organic gas in the atmosphere after methane (Jacob et al., 2005), with mixing ratios lying globally within the range 0.2–195 ppbv (Seco et al., 2007). At MSY methanol is found with the highest mixing ratios in both seasons (Fig. 8; Table 2). Its direct sources, as well as those of the other short-chain oxygenated VOCs, include emissions from the vegetation (Filella et al., 2009), soil, dead

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



plant matter, as well as anthropic sources such as biomass and fossil fuel combustion and industrial processes. In addition, oxVOCs can be formed secondarily as products of reactions of other – biogenic or anthropogenic – hydrocarbons of higher molecular weight. This is in fact the major atmospheric source of some of these oxVOCs, such as acetaldehyde (Seco et al., 2007). So, the difference in oxVOC mixing ratios between seasons may be attributed mainly to two phenomena: (i) the larger biogenic emissions in summer due to the increased physiological activity of vegetation, and (ii) increased secondary production in summer due to greater photochemical reactivity as a result of the higher temperatures and insolation. These compounds are characterized by a variety of atmospheric lifetimes, which span from over 10 days for acetone and methanol (Jacob et al., 2005; Singh et al., 2004) to a few hours for acetaldehyde (Possanzini et al., 2002). This may be the reason why acetone and methanol had the highest mixing ratios in this group, even at night, and also why acetaldehyde showed the lowest mixing ratios of all the oxVOCs measured (Fig. 8).

#### 4.1.2 Isoprenoids

It is generally considered that the main atmospheric source of isoprenoid VOCs is direct emission from vegetation (Guenther et al., 1995). As in the case of oxVOCs, increased emission rates of plants concurring with higher temperatures and radiation must be the reason for the great rise in their mixing ratios in summer compared to winter, which was the highest rise monitored in MSY (a 10- to 21-fold increase; Figs. 6 and 8; Table 2). Likewise, isoprenoid leaf-level emissions by *Q. ilex* measured during the campaign showed a similar increase of approximately one order of magnitude (Llusà et al., 2011). In this case, however, increased photochemistry would inhibit their mixing ratios increase, as these isoprenoids are far more reactive in the atmosphere than short-chain oxCOVs (Atkinson, 2000). Hence the vegetation source must have been stronger than the photochemical sink in summer.

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 4.1.3 Aromatic VOCs

Aromatic VOCs did not change substantially in mixing ratios between winter and summer at MSY (Figs. 7 and 8; Table 2), suggesting their emission sources are of similar strength all year round. Also, there are few sources of these compounds – mainly tailpipe exhaust – in the local environment of the MSY site, probably restricted to a little road in the valley and some small villages. Therefore their mixing ratios in MSY are assumed to come from relatively distant sources outside the valley. The aromatic VOC with the largest seasonal variation was benzene (winter levels doubled those of summer, see Table 2) but at the same time it was the aromatic VOC with less daily fluctuation (Fig. 7). The latter may be related to the fact that benzene has the longest atmospheric lifetime (in the order of days) among the aromatics measured (Atkinson, 2000) and for this reason it may be better mixed within the atmosphere.

### 4.1.4 Acetonitrile

Acetonitrile is considered a biomass burning marker (Holzinger et al., 1999), given that its main global source (94 %) is biomass burning, with only a minor part (less than 6 %) arising from fossil fuel combustion (Holzinger et al., 2001a). Similarly to benzene, its relatively long atmospheric lifetime (Sanhueza et al., 2004) may yield good acetonitrile mixing in the atmosphere, and as a consequence small daily variations of the mixing ratios (Fig. 8). In contrast with benzene, at MSY acetonitrile mixing ratio was double in summer compared to winter (Table 2).

## 4.2 Daily cycles and wind regime

Mixing ratios of all VOCs at this forested site showed a marked diel cycle in both seasons, and a very similar pattern, in most cases, within one particular season. This is particularly apparent in winter, when on average all VOC levels except monoterpenes – and to a lesser extent, acetonitrile – rose at the same time in morning, had almost

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**The effect of local biogenic emissions**

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

simultaneous peaks and decayed at the same moment in the evening (Fig. 8). Even the aromatic compounds followed this behaviour, despite having few local sources in the MSY valley. This common pattern indicates that the VOC mixing ratios measured at the site are mainly governed by the wind regime of the mountain. In winter, after sunrise the sea breeze starts to blow mountain upwards and VOC mixing ratios slightly increase, and about 2 h after that, they undergo a sharp increase. VOC levels are then maintained more or less constant until the wind changes direction and reduces speed, when at around 17:00 h GMT the sea breeze stops and the mountain drainage flow towards the valley starts instead. This general daily cycle of VOC mixing ratios driven by the wind is also observed in summertime. Such behaviour of atmospheric pollutants has been described elsewhere (Perez et al., 2008) and also for the same period of our study when comparing PM levels in the city of Barcelona and MSY (Pandolfi et al., 2011). In this case, the levels of fine particulate matter ( $PM_{10}$ ) increased in MSY when corresponding levels in Barcelona decreased. This was partly attributed to the mountain and sea breeze transport toward the MSY site.

Both biogenic and anthropogenic emissions of gaseous and particulate matter accumulate in the valleys and depressions (including the Barcelona metropolitan area) during the night and early morning. Later in the morning the air masses from the Barcelona metropolitan area are advected to MSY by the sea and mountain breezes, passing over further heavily industrialized areas, with some cities in the range of 50 000–100 000 inhabitants and a number of highways, and hence taking up more pollutants. At the same time, photochemical reactions take place within the air mass (e.g. ozone production, VOC degradation, etc.), so the pollution plume is aged when it reaches MSY.

While the ozone concentration at MSY is the result of photochemical production that has occurred over several hours (Sillman, 1999), in addition this air mass which is transported inland, loaded with a variety of anthropogenic pollutants (including VOCs), mixes at the forested site with new biogenic VOCs. This mixing process with VOCs produced locally at the valley where MSY is located may enhance ozone production (Calfapietra et al., 2009; Peñuelas and Staudt, 2010). Ozone production depends on



**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the VOC/NO<sub>x</sub> ratio of the air, and the MSY valley atmosphere in the early morning has NO<sub>x</sub>-sensitive conditions, that may change to more favorable conditions for ozone production when the breeze advects NO<sub>x</sub> from the metropolitan area. This could partially explain the higher ozone concentration found in MSY (means of 75 μg m<sup>-3</sup> at night and 90–125 μg m<sup>-3</sup> by day) compared to Barcelona city in both seasons (means of 40–50 μg m<sup>-3</sup> at night and 60–70 μg m<sup>-3</sup> at day; Pandolfi et al., 2011, as several reports have highlighted in other coastal-mountainous areas (Evyugina et al., 2006; Millan et al., 1997). Likewise, in the metropolitan area of Barcelona, at a NO<sub>x</sub>-rich semi-urban site (i.e. very similar to the areas upwind of MSY during the daytime) with high influence of urban, industrial and highway pollution, ozone levels measured were lower (means of 10–20 μg m<sup>-3</sup> at night and 50–90 μg m<sup>-3</sup> by day) than in MSY in both seasons (Filella and Peñuelas, 2006a). Furthermore, other studies have reported that ozone concentrations increase with altitude at mountain sites too (Diaz-de-Quijano et al., 2009; Evyugina et al., 2009; Ribas and Peñuelas, 2006). Of course another important cause of these higher ozone levels in the mountains is the lack of fresh NO emissions. In urban and semi urban environments the consumption of O<sub>3</sub> by freshly emitted NO to form NO<sub>2</sub> represents an important sink for ozone. In addition, VOC mixing ratios in summer, especially those of isoprenoids, were much higher than in winter and this together with a higher solar radiation and temperature promoting photochemical reactions, may partly explain the higher daytime ozone concentrations registered in summer.

Monoterpenes are a special case as regards this airborne VOC transport from polluted areas. In winter and summer, monoterpene mixing ratios started to rise earlier than the other VOCs, as soon as solar radiation started to increase too (Fig. 8), and this was probably due to the local origin of monoterpenes. Monoterpenes were emitted by holm oaks which densely populate the MSY site and the valley just beneath. Holm oaks are known monoterpene emitters (Kesselmeier and Staudt, 1999; Llusia and Peñuelas, 2000; Peñuelas and Llusia, 1999a), as confirmed by leaf-level measurements performed at MSY during this campaign (Llusia et al., 2011). The case of

**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



isoprene was, however, different. Although it is normally considered a biogenic VOC, it has also known anthropic sources, like automobile exhaust (Borbon et al., 2001), while in the case of monoterpenes anthropic origins are scarce. The difference in the mean wintertime diel cycle between isoprene and monoterpenes reflected in Fig. 8 may be indicative that most of the isoprene detected in winter was also advected to MSY and maybe a considerable amount was anthropogenic. A previous study in an semi-urban area in the metropolitan region of Barcelona (upwind of MSY) described this dominance of the human-related sources of isoprene in winter (Filella and Peñuelas, 2006b). In addition, winter monoterpene emissions by the valley oaks were low (Llusia et al., 2011), as reflected in the low mixing ratios reported. Thus isoprene emission must have been even lower because the emission of isoprene has been reported to be less than 5% of the emission of monoterpenes for this evergreen tree species (Peñuelas et al., 2009). Of course we can not rule out the possibility that different plant species of the vegetation found in the trajectory of the air masses as they were advected by the sea breeze (i.e. before entering the MSY valley) were responsible for loading those air masses with isoprene. Following this reasoning, in summer part of the isoprene at MSY may have also been anthropogenic, however the biogenic contribution either from distant vegetation (advected, see Filella and Peñuelas, 2006b) and from valley (local) isoprene-emitting species other than *Q. ilex* would have been greater. Moreover, isoprene in summer did not follow so closely the daily cycles of aromatics or oxVOCs as in winter, and instead had an earlier rise in mixing ratios, at the same time as monoterpenes did (Fig. 8). This may clearly indicate isoprene's summertime local biotic origin, at least in part. In contrast, most other VOCs including isoprene's oxidation products MVK and MACR started to rise collectively with a certain delay, when air masses advected by the sea breeze contributed to the VOC burden at MSY.

The only two other VOCs that also showed an early rise in the morning were methanol and toluene. On the one hand, methanol has been reported to build up inside the leaves of plants when stomata remain closed during the night, and then

burst out when they open in the morning. This phenomenon is under the control of the gas-liquid phase equilibrium of the alcohol within the leaf and of the stomatal conductance (Filella and Peñuelas, 2006b; Filella et al., 2009; Niinemets and Reichstein, 2003). Some authors described this morning burst in mixing ratios, and attributed it to this stomata-related response and to the evaporation of dew, supposing that methanol may be dissolved in it (Filella and Peñuelas, 2006b; Holzinger et al., 2001b; Sanhueza et al., 2001; Warneke et al., 2002). On the other hand, toluene has been reported to be emitted by plants (Heiden et al., 1999; White et al., 2009) and emissions of  $m/z$  93 have been reported for *Q. ilex* and attributed to toluene (Holzinger et al., 2000). However, the possibility that certain monoterpene fragments may contribute to  $m/z$  93 and thus being mistaken for toluene has been suggested (Kim et al., 2010). Notwithstanding, Ambrose et al. (2010) has recently reported this interference to be practically insignificant.

The high influence of the wind regime on VOC mixing ratios at MSY is illustrated by Fig. 9, which contains the same information as Fig. 8 but corresponds only to the 6 August, as representative for the atmospheric conditions of a number of days. On 6 August all VOCs, including monoterpenes, saw a reduction in mixing ratios when at around 14:00–15:00 h the wind started to change speed and moreover change direction, turning from SE (around 120 degrees) to W (260–270 degrees). Solar radiation did not change (e.g. due to clouds), so it is probable that local biogenic emissions did not decrease. This VOC mixing ratio reduction occurred simultaneously with a reduction in  $\text{NO}_2$  levels and a small increase in  $\text{O}_3$  concentration. At around 17:00 h the wind went back to SE direction briefly and then changed at 18:00 h to N for the whole night. VOC and  $\text{NO}_2$  concentrations increased again when the wind direction returned to the SE direction, and sharply decreased when it changed to N. The SE wind direction corresponded to the usual sea breeze that occurs at MSY, with the wind coming valley upwards from the Barcelona metropolitan region. When the wind was blowing from the W, the air was coming from another valley, and although *Q. ilex* is the dominant plant species there too, before arriving at the MSY site the air passed over Pla

**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



de la Calma (1100–1300 m a.s.l.), a plateau covered by heath communities of *Calluna vulgaris*, *Pteridium aquilinum*, *Festuca ovina*, and *Scleranthus annuus* (Bolòs, 1983). This different vegetation, much less dense and with less biomass, probably emits much less VOCs than the holm oak forests of the SE valley.

### 4.3 Comparison with VOC mixing ratios reported in the literature

Data on VOC mixing ratios from several other natural environments have also been reported (see Supplement for more details). In general, in Nordic environments oxVOC and isoprenoid mixing ratios were lower than those measured at MSY, with only some occasional peaks higher than at MSY (Holst et al., 2010; Lappalainen et al., 2009; Rinne et al., 2005; Ruuskanen et al., 2009). These results are in accordance with lower photochemical activity and also the lower physiological activity of the vegetation in Nordic regions, thus resulting in lower emissions compared to the Mediterranean MSY. In a rural area near the coast in New Hampshire (East USA), the oxVOC mixing ratios were also generally lower than at MSY in both seasons, while isoprenoids were in the same range or slightly higher than at MSY (Jordan et al., 2009). A mixed forest in the northern USA presented lower monoterpene mixing ratios than at MSY in summer, but higher isoprene mixing ratios (Mielke et al., 2010). The same situation for monoterpenes and isoprene compared to MSY was found in a mixed forest in NW Germany in summer, where methanol presented higher mixing ratios too (Spirig et al., 2005).

The only reports related to typical Mediterranean ecosystems are those from the Castelporziano site (Italy), surrounded by *Q. ilex* forests and macchia, and also influenced by the urban environment of Rome. For the year 1994 and within the BEMA campaign, Kalabokas et al. (1997) described a lower daily mean acetone mixing ratio (1.74 ppbv) than in MSY summer. However, that campaign was held in May and this mixing ratio is, accordingly, between our MSY winter and summer values. In contrast, the daily average mixing ratios of acetaldehyde (1.8 ppbv) were above those registered at MSY. More recently in 2007, Davison et al. (2009) took measurements again at the same site and period (May–June). The reported mixing ratios of methanol (medians of 1.6 to 3.5 ppbv) and again acetone (0.96–2.1 ppbv) were in this case slightly

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 lower than those at MSY, while acetaldehyde showed similar values (medians of 0.44–1.3 ppbv). Regarding isoprenoids, the mediterranean site of Castelporziano showed slightly lower mixing ratios of isoprene (medians of 0.1–0.37 ppbv) and MVK/MACR (medians of 0.13–0.30 ppbv) and clearly lower monoterpene mixing ratios (medians of 0.13–0.3) in May than at MSY in summer (Davison et al., 2009; Kalabokas et al., 1997). As with oxVOCs, the results for isoprenoids in summer in Castelporziano may have been hypothetically closer to those from MSY, as these mixing ratios are somewhat in between the MSY winter and summer readings. Nevertheless summer drought may exert a big influence in VOC emissions in Castelporziano and have the contrary effect, as the authors pointed out when choosing the period for measurements (they considered that plants would have good temperature and water conditions for VOC emission in May–June).

10 An interesting detail is that the maximum monoterpene mixing ratios in the 2007 Castelporziano campaign were detected at night, when the land breeze originated and air was coming from oak and pine forests. These mixing ratios were higher (medians of 0.26 to 0.57 ppbv) than the night ones at MSY. The authors attributed this behaviour to the nighttime temperature-dependent emissions of stored monoterpenes by the pines together with the cessation of photochemical destruction of VOCs and the suppression of vertical mixing at night (Davison et al., 2009). In MSY, vertical mixing and photo-chemistry were also suppressed at night, but the land breeze acted in the contrary sense, cleaning the air from VOCs. This may be in part due to the fact that there are no significant tree populations in the surroundings that could emit monoterpenes from storage pools at night, as holm oaks do not store monoterpenes. Rather they emit them from de novo synthesis, influenced by temperature, irradiance and water availability (Llusià and Peñuelas, 1999; Loreto et al., 1998; Peñuelas and Llusià, 1999b; Staudt et al., 2002). It should be noted that some forest measurements at Hyytiälä, Finland (Rinne et al., 2005; Ruuskanen et al., 2009), at a rural location in New Hampshire, USA (Jordan et al., 2009) and at a mixed forest in Germany (Mielke et al., 2010) also reported higher monoterpene mixing ratios in summer at night.

**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 5 Summary and conclusions

VOC mixing ratio measurements in an elevated Mediterranean forested site (MSY) with a dense vegetation dominated by *Quercus ilex* were performed. There were two sets of measures, one in winter (February–March) and another in summer (July–August).

While aromatic VOCs showed almost no seasonal variability (only benzene had lower summer mixing ratios), short-chain oxygenated VOCs presented higher mixing ratios in summer, presumably due to the increased emission by vegetation and increased photochemistry, both enhanced by the high temperatures and solar radiation in summer. Methanol was the most abundant compound among all the VOCs measured in both seasons.

Isoprenoid VOCs (monoterpenes and isoprene, and its oxidation products MVK/MACR) were involved in the biggest change in mixing ratios between winter and summer. That is, their mixing ratios increased by one order of magnitude, as a result of the increased physiological activity and emission rates of the vegetation. The highest diurnal concentrations of ozone increased in summer too, most likely due to more intense photochemical activity and the presence of more reactive VOCs in the air.

VOC mixing ratios analysis at the MSY forest site in the Western Mediterranean Basin showed that their diel variation is mainly governed by the wind regime of the mountain, since the majority of the VOC species analyzed followed a very similar daily cycle. Sea and mountain breezes that develop after sunrise advect polluted air masses to the mountain that previously had passed over the Barcelona metropolitan region, where they were enriched in  $\text{NO}_x$  and in VOCs of anthropic and biotic origin. Furthermore, these polluted air masses can react with biogenic VOCs emitted at the MSY valley by the vegetation, thus enhancing  $\text{O}_3$  formation in this mountain site. The only VOC species that showed a distinct different daily pattern – though still affected by the wind regime – were monoterpenes, because they were emitted by the local vegetation of the valley. Isoprene also shared partially the diel pattern of the monoterpenes, but only in summer when its biotic sources were stronger. These high concentrations of

### The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



biogenic volatile isoprenoids indicate the significant impact of local forested vegetation on air quality in these Mediterranean areas which also receive polluted air masses from anthropic sources.

**Supplementary material related to this article is available online at:**

**[http://www.atmos-chem-phys-discuss.net/11/20389/2011/  
acpd-11-20389-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/20389/2011/acpd-11-20389-2011-supplement.pdf)**

*Acknowledgements.* This study was supported by the Spanish Government grants CGL2006-04025/BOS, CGL2010-17172, Consolider-Ingenio Montes CSD2008-00040 and Acción Complementaria DAURE CGL2007-30502-E/CLI, and the Catalan Government grant SGR 2009-458. Roger Seco gratefully acknowledges an FPI fellowship (BES-2005-6989) from the Spanish Government.

This research has received funding from the EC Seventh Framework Programme under grant agreement no. 215072 (Marie Curie Initial Training Network, "CLOUD-ITN"). Helpful discussion concerning the PTR-TOF evaluation with Martin Graus and Ralf Schnitzhofer from the University of Innsbruck was much appreciated.

## References

- Ambrose, J. L., Haase, K., Russo, R. S., Zhou, Y., White, M. L., Frinak, E. K., Jordan, C., Mayne, H. R., Talbot, R., and Sive, B. C.: A comparison of GC-FID and PTR-MS toluene measurements in ambient air under conditions of enhanced monoterpene loading, *Atmos. Meas. Tech.*, 3, 959–980, doi:10.5194/amt-3-959-2010, 2010.
- Arneth, A., Harrison, S. P., Zaehle, S., Tsigaridis, K., Menon, S., Bartlein, P. J., Feichter, J., Korhola, A., Kulmala, M., O'Donnell, D., Schurgers, G., Sorvari, S., and Vesala, T.: Terrestrial biogeochemical feedbacks in the climate system, *Nature Geosci.*, 3, 525–532, 2010.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO<sub>x</sub>, *Atmos. Environ.*, 34, 2063–2101, 2000.
- Avila, A. and Alarcon, M.: Precipitation chemistry at a rural Mediterranean site: Between

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



anthropogenic pollution and natural emissions, *J. Geophys. Res.-Atmos.*, 108, 4278, doi:10.1029/2002JD002565, 2003.

Avila, A. and Rodà, F.: Assessing decadal changes in rainwater alkalinity at a rural Mediterranean site in the Montseny Mountains (NE Spain), *Atmos. Environ.*, 36, 2881–2890, 2002.

5 Avila, A. and Rodrigo, A.: Trace metal fluxes in bulk deposition, throughfall and stemflow at two evergreen oak stands in NE Spain subject to different exposure to the industrial environment, *Atmos. Environ.*, 38, 171–180, 2004.

Avila, A., Alarcon, M., and Queralt, I.: The chemical composition of dust transported in red rains – Its contribution to the biogeochemical cycle of a Holm oak forest in Catalonia (Spain), *Atmos. Environ.*, 32, 179–191, 1998.

10 Avila, A., Rodrigo, A., and Rodà, F.: Nitrogen circulation in a Mediterranean holm oak forest, La Castanya, Montseny, northeastern Spain, *Hydrol. Earth Syst. Sci.*, 6, 551–558, doi:10.5194/hess-6-551-2002, 2002.

Avila, A., Alarcon, M., Castillo, S., Escudero, M., Garcia-Orellana, J., Masque, P., and Querol, X.: Variation of soluble and insoluble calcium in red rains related to dust sources and transport patterns from North Africa to northeastern Spain, *J. Geophys. Res.-Atmos.*, 112, D05210, doi:10.1029/2006JD007153, 2007.

Avila, A., Molowny-Horas, R., Gimeno, B. S., and Peñuelas, J.: Analysis of Decadal Time Series in Wet N Concentrations at Five Rural Sites in NE Spain, *Water Air Soil Pollut.*, 207, 123–138, 2010.

20 Baldwin, I. T., Halitschke, R., Paschold, A., von Dahl, C. C., and Preston, C. A.: Volatile signaling in plant-plant interactions: “Talking trees” in the genomics era, *Science*, 311, 812–815, 2006.

Bolòs, O. D.: *La vegetació del Montseny*, Diputació de Barcelona, Barcelona, 1983.

25 Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J. C. and Guillermo, R.: An investigation into the traffic-related fraction of isoprene at an urban location, *Atmos. Environ.*, 35, 3749–3760, 2001.

Calfapietra, C., Fares, S., and Loreto, F.: Volatile organic compounds from Italian vegetation and their interaction with ozone, *Environ. Pollut.*, 157, 1478–1486, 2009.

30 Davison, B., Taipale, R., Langford, B., Misztal, P., Fares, S., Matteucci, G., Loreto, F., Cape, J. N., Rinne, J., and Hewitt, C. N.: Concentrations and fluxes of biogenic volatile organic compounds above a Mediterranean macchia ecosystem in western Italy, *Biogeosciences*, 6, 1655–1670, doi:10.5194/bg-6-1655-2009, 2009.

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, 26, 223–257, 2007.

Diaz-de-Quijano, M., Peñuelas, J., and Ribas, A.: Increasing interannual and altitudinal ozone mixing ratios in the Catalan Pyrenees, *Atmos. Environ.*, 43, 6049–6057, 2009.

Evyugina, M. G., Nunes, T., Pio, C., and Costa, C. S.: Photochemical pollution under sea breeze conditions, during summer, at the Portuguese West Coast, *Atmos. Environ.*, 40, 6277–6293, 2006.

Evyugina, M. G., Nunes, T., Alves, C., and Marques, M. C.: Photochemical pollution in a rural mountainous area in the northeast of Portugal, *Atmos. Res.*, 92, 151–158, 2009.

Filella, I. and Peñuelas, J.: Daily, weekly and seasonal relationships among VOCs, NO<sub>x</sub> and O<sub>3</sub> in a semi-urban area near Barcelona, *J. Atmos. Chem.*, 54, 189–201, 2006a.

Filella, I. and Peñuelas, J.: Daily, weekly, and seasonal time courses of VOC concentrations in a semi-urban area near Barcelona, *Atmos. Environ.*, 40, 7752–7769, 2006b.

Filella, I., Peñuelas, J., and Seco, R.: Short-chained oxygenated VOC emissions in *Pinus halepensis* in response to changes in water availability, *Acta Physiol. Plant.*, 31, 311–318, 2009.

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S. A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neiryneck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Røpoulsen, H., Cellier, P., Cape, J. N., Horvath, L., Loreto, F., Niinemets, U., Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüeggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N., and Erisman, J. W.: Atmospheric composition change: Ecosystems-Atmosphere interactions, *Atmos. Environ.*, 43, 5193–5267, 2009.

Gimeno, B. S., Peñuelas, J., Porcuna, J. L., and Reinert, R. A.: Biomonitoring ozone phytotoxicity in eastern Spain, *Water Air Soil Pollut.*, 85, 1521–1526, 1995.

Graus, M., Müller, M., and Hansel, A.: High Resolution PTR-TOF: Quantification and Formula Confirmation of VOC in Real Time, *J. Am. Soc. Mass Spectrom.*, 21, 1037–1044, 2010.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor,

## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



J., and Zimmerman, P.: A Global-Model of Natural Volatile Organic-Compound Emissions, *J. Geophys. Res.*, 100, 8873–8892, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., Shao, M., and Wildt, J.: Toluene emissions from plants, *Geophys. Res. Lett.*, 26, 1283–1286, 1999.

Heil, M. and Kost, C.: Priming of indirect defences, *Ecol. Lett.*, 9, 813–817, 2006.

Holzinger, R., Warneke, C., Hansel, A., Jordan, A., Lindinger, W., Scharffe, D. H., Schade, G., and Crutzen, P. J.: Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, *Geophys. Res. Lett.*, 26, 1161–1164, 1999.

Holzinger, R., Sandoval-Soto, L., Rottenberger, S., Crutzen, P. J., and Kesselmeier, J.: Emissions of volatile organic compounds from *Quercus ilex* L. measured by Proton Transfer Reaction Mass Spectrometry under different environmental conditions, *J. Geophys. Res.*, 105, 20573–20579, 2000.

Holzinger, R., Jordan, A., Hansel, A., and Lindinger, W.: Automobile emissions of acetonitrile: Assessment of its contribution to the global source, *J. Atmos. Chem.*, 38, 187–193, 2001a.

Holzinger, R., Jordan, A., Hansel, A., and Lindinger, W.: Methanol measurements in the lower troposphere near Innsbruck (047 degrees 16' N; 011 degrees 24' E), Austria, *Atmos. Environ.*, 35, 2525–2532, 2001b.

Holst, T., Arneith, A., Hayward, S., Ekberg, A., Mastepanov, M., Jackowicz-Korczynski, M., Friberg, T., Crill, P. M., and Bäckstrand, K.: BVOC ecosystem flux measurements at a high latitude wetland site, *Atmos. Chem. Phys.*, 10, 1617–1634, doi:10.5194/acp-10-1617-2010, 2010.

Jacob, D. J., Field, B. D., Li, Q. B., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H. B., and Guenther, A.: Global budget of methanol: Constraints from atmospheric observations, *J. Geophys. Res.*, 110, D08303, doi:10.1029/2004JD005172, 2005.

Jordan, C., Fitz, E., Hagan, T., Sive, B., Frinak, E., Haase, K., Cottrell, L., Buckley, S., and Talbot, R.: Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences, *Atmos. Chem. Phys.*, 9, 4677–4697, doi:10.5194/acp-9-4677-2009, 2009.

Kalabokas, P., Bartzis, J. G., Bomboi, T., Ciccioli, P., Cieslik, S., Dlugi, R., Foster, P., Kotzias,

**The effect of local biogenic emissions**

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

D., and Steinbrecher, R.: Ambient atmospheric trace gas concentrations and meteorological parameters during the first BEMA measuring campaign on May 1994 at Castelporziano, Italy, *Atmos. Environ.*, 31, 67–77, 1997.

Karl, T., Guenther, A., Jordan, A., Fall, R., and Lindinger, W.: Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting, *Atmos. Environ.*, 35, 491–495, 2001.

Karl, T., Hansel, A., Mark, T., Lindinger, W., and Hoffmann, D.: Trace gas monitoring at the Mauna Loa Baseline observatory using proton-transfer reaction mass spectrometry, *Int. J. Mass Spectrom.*, 223, 527–538, 2003.

Kavouras, I. G., Mihalopoulos, N., and Stephanou, E. G.: Formation of atmospheric particles from organic acids produced by forests, *Nature*, 395, 683–686, 1998.

Kegge, W. and Pierik, R.: Biogenic volatile organic compounds and plant competition, *Trends Plant Sci.*, 15, 126–132, 2010.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, *J. Atmos. Chem.*, 33, 23–88, 1999.

Kessler, A. and Baldwin, I. T.: Defensive function of herbivore-induced plant volatile emissions in nature, *Science*, 291, 2141–2144, 2001.

Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra, *Atmos. Chem. Phys.*, 10, 1759–1771, doi:10.5194/acp-10-1759-2010, 2010.

Kulmala, M., Suni, T., Lehtinen, K. E. J., Dal Maso, M., Boy, M., Reissell, A., Rannik, Ü., Aalto, P., Keronen, P., Hakola, H., Bäck, J., Hoffmann, T., Vesala, T., and Hari, P.: A new feedback mechanism linking forests, aerosols, and climate, *Atmos. Chem. Phys.*, 4, 557–562, doi:10.5194/acp-4-557-2004, 2004.

Lappalainen, H. K., Sevanto, S., Bäck, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M., and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, *Atmos. Chem. Phys.*, 9, 5447–5459, doi:10.5194/acp-9-5447-2009, 2009.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) – Medical applications, food control and environmental research, *Int. J. Mass Spectrom.*, 173, 191–241, 1998.

**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Lippmann, M.: Health-Effects of Tropospheric Ozone – Review of Recent Research Findings and their Implications to Ambient Air-Quality Standards, *J. Expo. Anal. Environ. Epidemiol.*, 3, 103–129, 1993.

Llusià, J. and Peñuelas, J.: *Pinus halepensis* and *Quercus ilex* terpene emission as affected by temperature and humidity, *Biol. Plantarum*, 42, 317–320, 1999.

Llusià, J. and Peñuelas, J.: Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions, *Am. J. Bot.*, 87, 133–140, 2000.

Llusià, J. and Peñuelas, J.: Emission of volatile organic compounds by apple trees under spider mite attack and attraction of predatory mites, *Exp. Appl. Acarol.*, 25, 65–77, 2001.

Llusià, J., Peñuelas, J., Sardans, J., Owen, S. M., and Niinemets, Ü.: Measurement of volatile terpene emissions in 70 dominant vascular plant species in Hawaii: aliens emit more than natives, *Global Ecol. Biogeogr.*, 19, 863–874, 2010.

Llusià, J., Peñuelas, J., Seco, R., and Filella, I.: Seasonal changes in the daily terpene emission rates in *Quercus ilex* and in the terpene air concentrations in the natural park of Montseny, in preparation, 2011.

Loreto, F., Ciccioli, P., Brancaleoni, E., Valentini, R., De Lillis, M., Csiky, O., and Seufert, G.: A hypothesis on the evolution of isoprenoid emission by oaks based on the correlation between emission type and *Quercus* taxonomy, *Oecologia*, 115, 302–305, 1998.

Mielke, L. H., Pratt, K. A., Shepson, P. B., McLuckey, S. A., Wisthaler, A., and Hansel, A.: Quantitative Determination of Biogenic Volatile Organic Compounds in the Atmosphere Using Proton-Transfer Reaction Linear Ion Trap Mass Spectrometry, *Anal. Chem.*, 82, 7952–7957, 2010.

Millan, M. M., Salvador, R., Mantilla, E., and Kallos, G.: Photooxidant dynamics in the Mediterranean basin in summer: Results from European research projects, *J. Geophys. Res.-Atmos.*, 102, 8811–8823, 1997.

Niinemets, U. and Reichstein, M.: Controls on the emission of plant volatiles through stomata: Differential sensitivity of emission rates to stomatal closure explained, *J. Geophys. Res.*, 108, 4208, doi:10.1029/2002JD002620, 2003.

Pacifico, F., Harrison, S. P., Jones, C. D., and Sitch, S.: Isoprene emissions and climate, *Atmos. Environ.*, 43, 6121–6135, 2009.

Pandolfi, M., Querol, X., Alastuey, A., Jimenez, J. L., Cusack, M., Reche, C., Pey, J., Mohr, C., DeCarlo, P., Prévôt, A., Baltensperger, U., Artiñano, B., Baldasano, J. M., Jorba, O., Burkhardt, J., Hansel, A., Schallhart, S., Müller, M., Metzger, A., Ortega, A., Saarikoski, S.,

---

**The effect of local biogenic emissions**R. Seco et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Cubison, M., Ng, S., Lorente, J., Nemitz, E., di Marco, C., Peñuelas, J., Sicard, M., Comeron, A., Amato, F., Moreno, T., Viana, M., Pérez, N., Moreno, N., Seco, R., Filella, I., Llusà, J., Piot, M., and Pay, M. T.: Source and origin of PM in the Western Mediterranean Basin: An overview of the DAURE campaign, Atmos. Chem. Phys. Discuss., in preparation, 2011.

5 Peñuelas, J., Filella, I., Seco, R., and Llusà, J.: Increase in isoprene and monoterpene emissions after re-watering of droughted *Quercus ilex* seedlings, Biol. Plantarum, 53, 351–354, 2009.

Peñuelas, J. and Llusà, J.: Seasonal emission of monoterpenes by the Mediterranean tree *Quercus ilex* in field conditions: Relations with photosynthetic rates, temperature and volatility, Physiol. Plant., 105, 641–647, 1999a.

10 Peñuelas, J. and Llusà, J.: Short-term responses of terpene emission rates to experimental changes of PFD in *Pinus halepensis* and *Quercus ilex* in summer field conditions, Environ. Exp. Bot., 42, 61–68, 1999b.

Peñuelas, J. and Llusà, J.: Linking photorespiration, monoterpenes and thermotolerance in *Quercus*, New Phytol., 155, 227–237, 2002.

Peñuelas, J. and Munné-Bosch, S.: Isoprenoids: an evolutionary pool for photoprotection, Trends Plant Sci., 10, 166–169, 2005.

Peñuelas, J. and Staudt, M.: BVOCs and global change, Trends Plant Sci., 15, 133–144, 2010.

20 Peñuelas, J., Llusà, J., and Estiarte, M.: Terpenoids – a Plant Language, Trends Ecol. Evol., 10, 289–289, 1995.

Peñuelas, J., Llusà, J., Asensio, D., and Munné-Bosch, S.: Linking isoprene with plant thermotolerance, antioxidants and monoterpene emissions, Plant Cell Environ., 28, 278–286, 2005.

25 Perez, N., Pey, J., Castillo, S., Viana, M., Alastuey, A., and Querol, X.: Interpretation of the variability of levels of regional background aerosols in the Western Mediterranean, Sci. Total Environ., 407, 527–540, 2008.

Pey, J., Perez, N., Castillo, S., Viana, M., Moreno, T., Pandolfi, M., Lopez-Sebastian, J. M., Alastuey, A., and Querol, X.: Geochemistry of regional background aerosols in the Western Mediterranean, Atmos. Res., 94, 422–435, 2009.

30 Pichersky, E. and Gershenzon, J.: The formation and function of plant volatiles: perfumes for pollinator attraction and defense, Curr. Opin. Plant Biol., 5, 237–243, 2002.

Pierik, R., Visser, E. J. W., De Kroon, H., and Voeseek, L. A. C. J.: Ethylene is required in tobacco to successfully compete with proximate neighbours, Plant Cell Environ., 26, 1229–

1234, 2003.

Piñol, J., Avila, A., Escarre, A., Lledo, M. J., and Rodà, F.: Comparison of the Hydrological Characteristics of 3 Small Experimental Holm Oak Forested Catchments in Ne Spain in Relation to Larger Areas, *Vegetatio*, 100, 169–176, 1992.

Possanzini, M., Di Palo, V., and Cecinato, A.: Sources and photodecomposition of formaldehyde and acetaldehyde in Rome ambient air, *Atmos. Environ.*, 36, 3195–3201, 2002.

Ribas, A. and Peñuelas, J.: Temporal patterns of surface ozone levels in different habitats of the North Western Mediterranean basin, *Atmos. Environ.*, 38, 985–992, 2004.

Ribas, A. and Peñuelas, J.: Surface ozone mixing ratio increase with altitude in a transect in the Catalan Pyrenees, *Atmos. Environ.*, 40, 7308–7315, 2006.

Ribas, A., Peñuelas, J., Elvira, S., and Gimeno, B. S.: Ozone exposure induces the activation of leaf senescence-related processes and morphological and growth changes in seedlings of Mediterranean tree species, *Environ. Pollut.*, 134, 291–300, 2005.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, *Boreal Environ. Res.*, 10, 425–436, 2005.

Ruuskanen, T. M., Taipale, R., Rinne, J., Kajos, M. K., Hakola, H., and Kulmala, M.: Quantitative long-term measurements of VOC concentrations by PTR-MS: annual cycle at a boreal forest site, *Atmos. Chem. Phys. Discuss.*, 9, 81–134, doi:10.5194/acpd-9-81-2009, 2009.

Sanhueza, E., Holzinger, R., Donoso, L., Santana, M., Fernandez, E., and Romero, J.: Volatile organic compounds in the atmosphere of La Gran Sabana. I: Concentrations and atmospheric chemistry, *Interciencia*, 26, 597–605, 2001.

Sanhueza, E., Holzinger, R., Kleiss, B., Donoso, L., and Crutzen, P. J.: New insights in the global cycle of acetonitrile: release from the ocean and dry deposition in the tropical savanna of Venezuela, *Atmos. Chem. Phys.*, 4, 275–280, doi:10.5194/acp-4-275-2004, 2004.

Sanz, M. J., Calatayud, V., and Calvo, E.: Spatial pattern of ozone injury in Aleppo pine related to air pollution dynamics in a coastal–mountain region of eastern Spain, *Environ. Pollut.*, 108, 239–247, 2000.

Seco, R., Peñuelas, J., and Filella, I.: Short-chain oxygenated VOCs: Emission and uptake by plants and atmospheric sources, sinks, and concentrations, *Atmos. Environ.*, 41, 2477–2499, 2007.

Seco, R., Peñuelas, J., and Filella, I.: Formaldehyde emission and uptake by Mediterranean trees *Quercus ilex* and *Pinus halepensis*, *Atmos. Environ.*, 42, 7907–7914, 2008.

The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## The effect of local biogenic emissions

R. Seco et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Seco, R., Filella, I., Llusà, J., and Peñuelas, J.: Methanol as a signal triggering isoprenoid emissions and photosynthetic performance in *Quercus ilex*, *Acta Physiol. Plant.*, doi:10.1007/s11738-011-0782-0, in press, 2011.
- Sillman, S.: The relation between ozone, NO<sub>x</sub> and hydrocarbons in urban and polluted rural environments, *Atmos. Environ.*, 33, 1821–1845, 1999.
- Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, *J. Geophys. Res.*, 109, D15S07, doi:10.1029/2003JD003883, 2004.
- Singsaas, E. L. and Sharkey, T. D.: The regulation of isoprene emission responses to rapid leaf temperature fluctuations, *Plant Cell Environ.*, 21, 1181–1188, 1998.
- Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, *Atmos. Chem. Phys.*, 5, 465–481, doi:10.5194/acp-5-465-2005, 2005.
- Staudt, M., Rambal, S., Joffre, R., and Kesselmeier, J.: Impact of drought on seasonal monoterpene emissions from *Quercus ilex* in southern France, *J. Geophys. Res.-Atmos.*, 107, 4602, doi:10.1029/2001JD002043, 2002.
- Terradas, J.: Holm oak and holm oak forest: an introduction, in: *Ecology of Mediterranean evergreen oak forests*, edited by: Rodà, F., Retana, J., Gracia, C. A., and Bellot, J., Springer, Berlin, 3–14, 1999.
- Tunved, P., Hansson, H. C., Kerminen, V. M., Strom, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M.: High natural aerosol loading over boreal forests, *Science*, 312, 261–263, 2006.
- Velikova, V., Pinelli, P., Pasqualini, S., Reale, L., Ferranti, F., and Loreto, F.: Isoprene decreases the concentration of nitric oxide in leaves exposed to elevated ozone, *New Phytol.*, 166, 419–426, 2005.
- Warneke, C., Luxembourg, S. L., de Gouw, J. A., Rinne, H. J. I., Guenther, A., and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, *J. Geophys. Res.*, 107, 4067–4067, 2002.
- White, M. L., Russo, R. S., Zhou, Y., Ambrose, J. L., Haase, K., Frinak, E. K., Varner, R. K., Wingenter, O. W., Mao, H., Talbot, R., and Sive, B. C.: Are biogenic emissions a significant

source of summertime atmospheric toluene in the rural Northeastern United States?, Atmos. Chem. Phys., 9, 81–92, doi:10.5194/acp-9-81-2009, 2009.

Wright, G. A. and Schiestl, F. P.: The evolution of floral scent: the influence of olfactory learning by insect pollinators on the honest signalling of floral rewards, Funct. Ecol., 23, 841–851, 2009.

Zhao, J. and Zhang, R. Y.: Proton transfer reaction rate constants between hydronium ion ( $\text{H}_3\text{O}^+$ ) and volatile organic compounds, Atmos. Environ., 38, 2177–2185, 2004.

Ziomas, I. C.: The Mediterranean Campaign of Photochemical Tracers Transport and chemical evolution (MEDCAPHOT-TRACE): An outline, Atmos. Environ., 32, 2045–2053, 1998.

ACPD

11, 20389–20431, 2011

**The effect of local biogenic emissions**

R. Seco et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



## The effect of local biogenic emissions

R. Seco et al.

**Table 1.** Masses measured with the different PTR-MS systems and the corresponding VOC identity assigned to them. The mean sensitivity and the limit of detection for each VOC are also displayed. Sensitivities shown are transmission corrected and normalized to the primary ion signal, taking into account all major molecular fragments. Detection limits (DL) were inferred from a signal to noise ratio ( $S/N$ ) of 2 according to  $DL = 2 \times SD_{\text{blank}}/\text{sensitivity}$ , with  $SD_{\text{blank}}$  being the standard deviation of background concentrations, as reported elsewhere (Karl et al., 2003).

Assigned VOC identity	PTR-ToF-MS (winter)			PTR-Quad-MS (summer)		
	measured exact protonated mass	Sensitivity (ncps ppbv <sup>-1</sup> )	Limit of detection (ppbv) <sup>c</sup>	measured nominal protonated mass	Sensitivity (ncps ppbv <sup>-1</sup> )	Limit of detection (ppbv) <sup>d</sup>
Methanol	33.033	12.8	0.011	33	17.9 <sup>b</sup>	0.415
Ethanol	47.048	1.1	0.066	–	–	–
Ethanol/formic acid	–	–	–	47	16.2 <sup>b</sup>	0.092
Acetone	59.049	22.4	0.003	59	28.5 <sup>b</sup>	0.013
Acetaldehyde	45.033	22.4 <sup>a</sup>	0.010	45	28.5 <sup>b</sup>	0.036
Acetic acid	61.028	22.4 <sup>a</sup>	0.008	61	17.5 <sup>b</sup>	0.031
Isoprene	69.069	10.6	0.002	69	12.7 <sup>b</sup>	0.021
MVK/MACR	71.09	22.4 <sup>a</sup>	< 0.001	71	28.1 <sup>b</sup>	0.009
Monoterpenes	81.070 and 137.132	15.0	0.004	81 and 137	18.5 <sup>b</sup>	0.029
Benzene	79.054	12.5	0.001	79	16.9	0.008
Toluene	93.069	14.8	< 0.001	93	16.9	0.015
C-8 aromatics	107.085	16.2	< 0.001	107	15.9	0.010
Acetonitrile	42.033	22.6	0.001	42	19.2 <sup>b</sup>	0.013

<sup>a</sup> These sensitivities were not measured in calibrations, and acetone sensitivity was used instead.

<sup>b</sup> These sensitivities were not measured in calibrations, but calculated using proton transfer reaction rate coefficients and transmission coefficients.

<sup>c</sup> Calculated for a 30 min integration time.

<sup>d</sup> Calculated for an integration time of 2 s, except for mass 33 (0.5 s) and for masses  $\geq 107$  (5 s).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## The effect of local biogenic emissions

R. Seco et al.

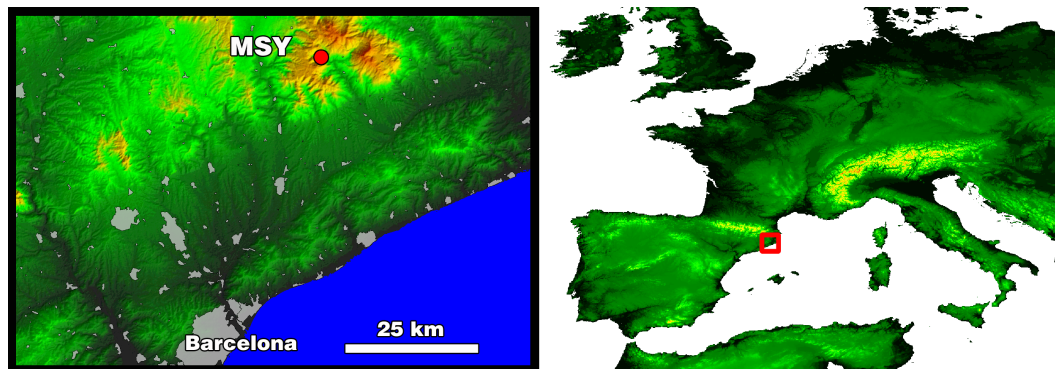
**Table 2.** Minimum and maximum VOC mixing ratios (ppbv) recorded at MSY station during the winter and summer campaigns.

VOC	WINTER				SUMMER			
	Minimum	Maximum	Hourly averages minimum	Hourly averages maximum	Minimum	Maximum	Hourly averages minimum	Hourly averages maximum
Methanol	0.256	9.761	1.279	2.704	1.410	13.400	4.142	6.053
Ethanol/formic acid	< 0.066	8.950	0.474	2.083	0.374	4.480	1.146	2.869
Acetone	0.257	3.897	0.787	1.547	0.967	5.950	2.260	3.834
Acetaldehyde	0.071	1.885	0.227	0.657	< 0.036	3.370	0.541	1.264
Isoprene	0.003	0.184	0.019	0.071	< 0.021	1.250	0.152	0.753
MVK/MACR	0.002	0.153	0.011	0.047	< 0.009	1.040	0.166	0.537
Monoterpenes	< 0.004	0.234	0.005	0.067	0.035	2.560	0.127	1.421
Acetic acid	0.026	5.348	0.393	1.428	0.270	5.640	1.317	2.940
Benzene	0.059	0.470	0.105	0.190	0.008	0.194	0.039	0.090
Toluene	0.001	1.903	0.057	0.408	< 0.015	1.340	0.083	0.467
C8-aromatics	0.003	1.328	0.031	0.249	< 0.010	0.821	0.091	0.272
Acetonitrile	0.027	0.258	0.075	0.101	0.037	0.588	0.159	0.216

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


**The effect of local biogenic emissions**

R. Seco et al.

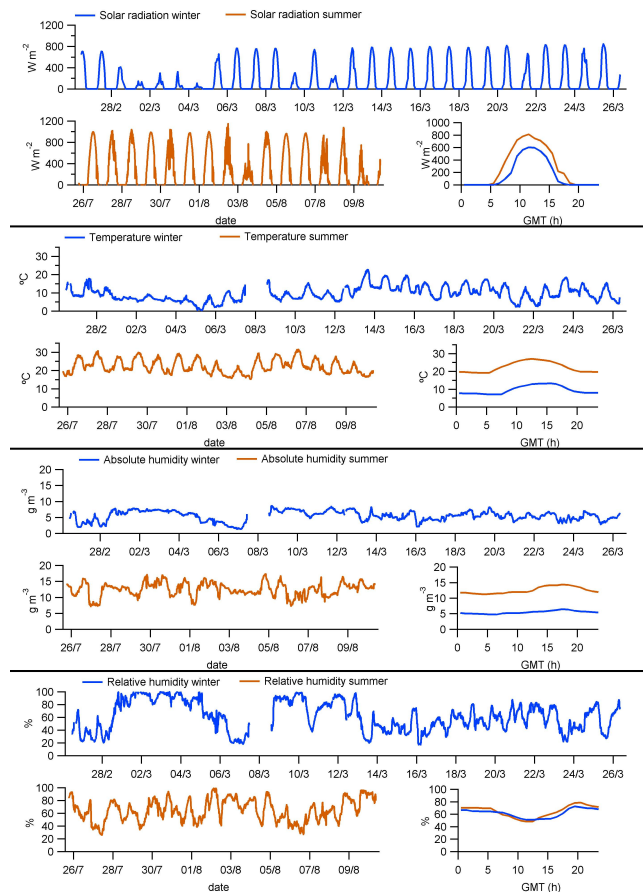


**Fig. 1.** Location of the Montseny (MSY) measurement site, in relation to the city of Barcelona.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## The effect of local biogenic emissions

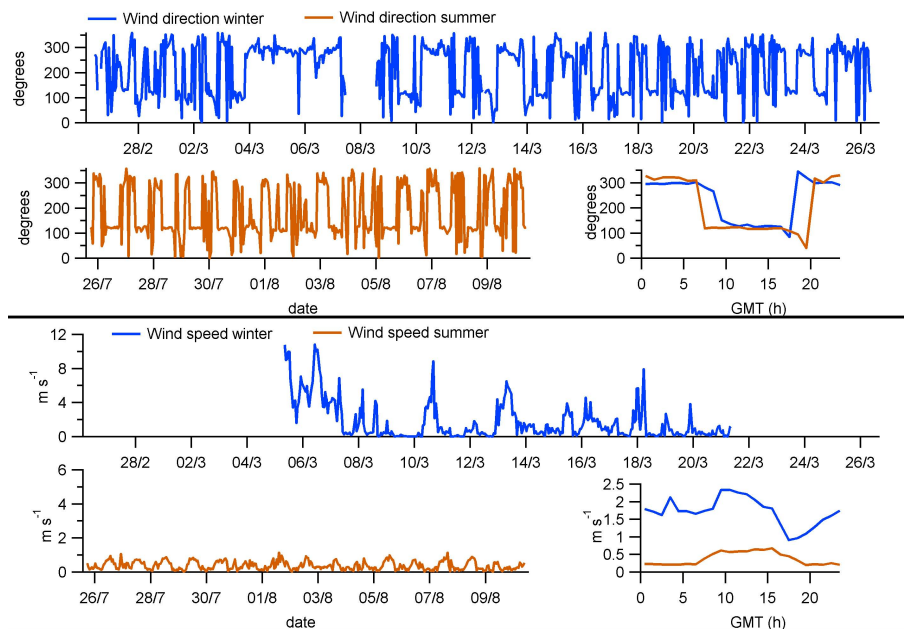
R. Seco et al.



**Fig. 2.** Solar radiation, temperature, and absolute and relative humidity during the winter period (upper graph of each panel), during the summer period (lower left graph) and their mean daily cycles (hourly averages) for both periods (lower right graph). Date labels indicate 00:00 GMT.

## The effect of local biogenic emissions

R. Seco et al.

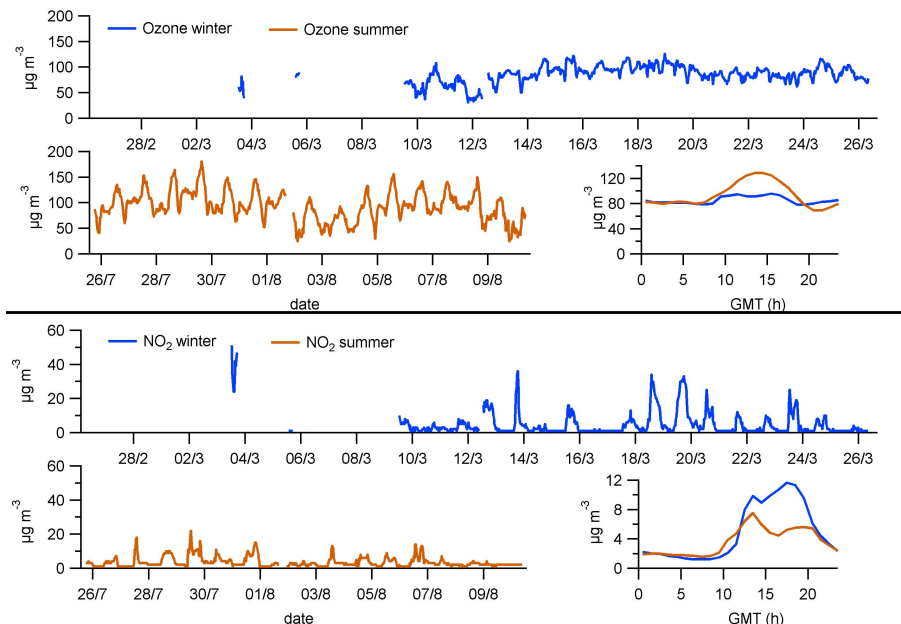


**Fig. 3.** Wind direction and speed during the winter period (upper graph of each panel), during the summer period (lower left graph) and their mean daily cycles (hourly averages) for both periods (lower right graph). Note the different scaling for graphs on wind speed seasonal trend graphs, however, also note that some problems were encountered with the recording software when measuring the wind speeds for summer. Thus the magnitudes displayed seem to be lower than the actual wind speeds of those days. Date labels indicate 00:00 GMT.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## The effect of local biogenic emissions

R. Seco et al.

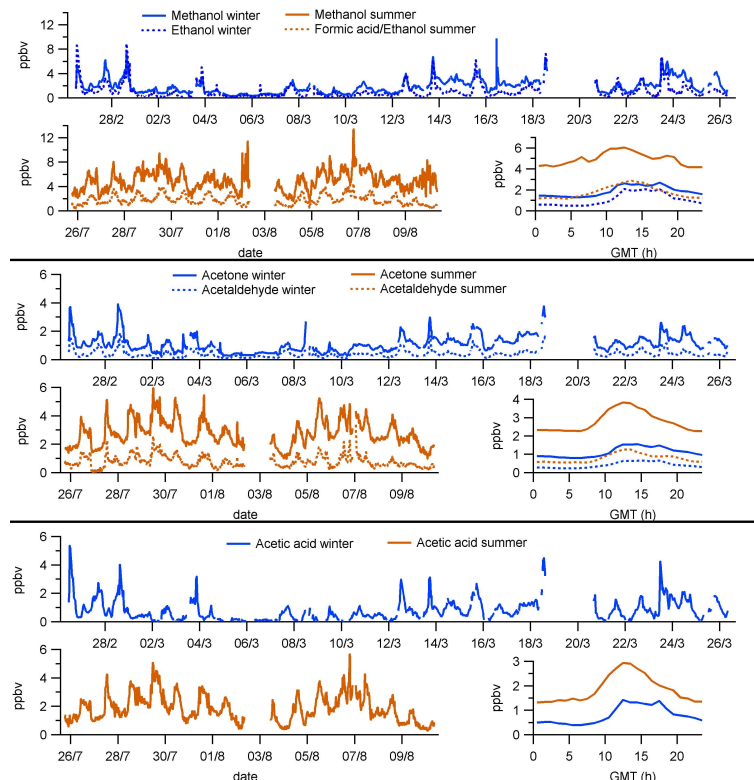


**Fig. 4.** Ozone and nitrogen dioxide concentrations during the winter period (upper graph of each panel), during the summer period (lower left graph) and their mean daily cycles (hourly averages) for both periods (lower right graph). Date labels indicate 00:00 GMT.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## The effect of local biogenic emissions

R. Seco et al.



**Fig. 5.** Short-chain oxygenated VOCs measured at MSY, showing their mixing ratios during the winter period (upper graph of each panel), their mixing ratios during the summer period (lower left graph) and their mean daily cycles (hourly averages) for both periods (lower right graph). Date labels indicate 00:00 GMT.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

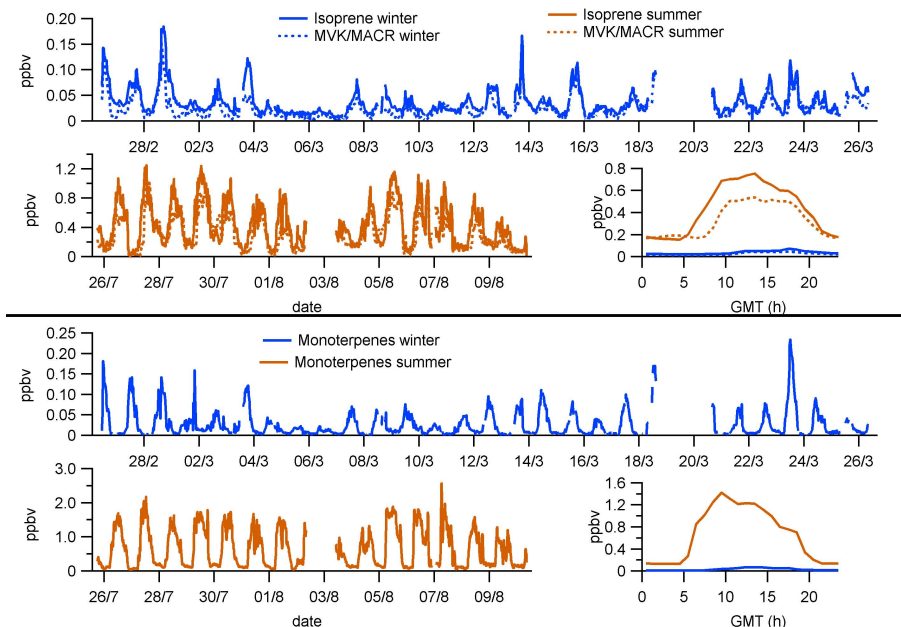
Printer-friendly Version

Interactive Discussion



## The effect of local biogenic emissions

R. Seco et al.



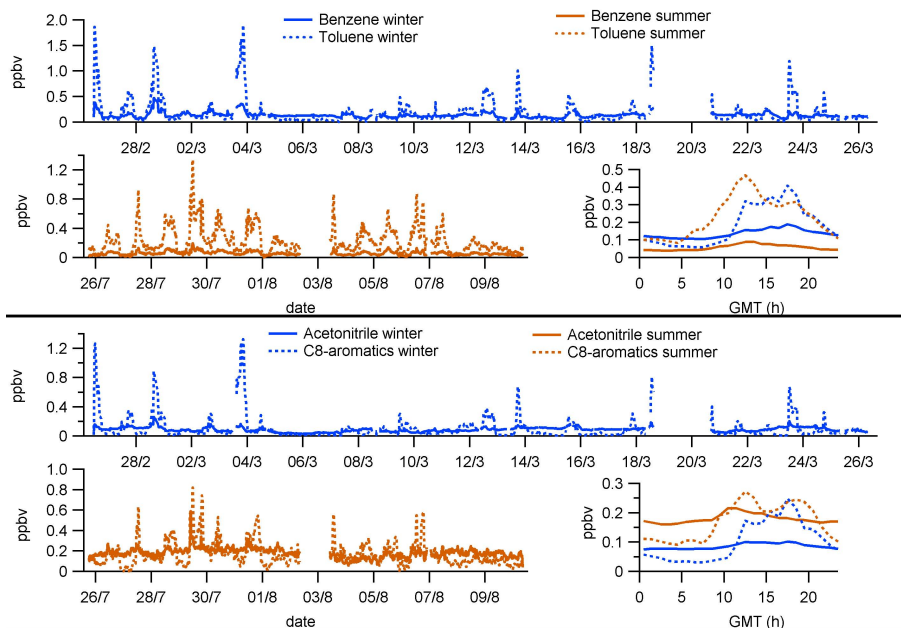
**Fig. 6.** Isoprenoid VOCs and MVK/MACR measured at MSY, showing their mixing ratios during the winter period (upper graph of each panel), their mixing ratios during the summer period (lower left graph) and their mean daily cycles (hourly averages) for both periods (lower right graph). Note the different scaling for the seasonal trend graphs. Date labels indicate 00:00 GMT.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



## The effect of local biogenic emissions

R. Seco et al.

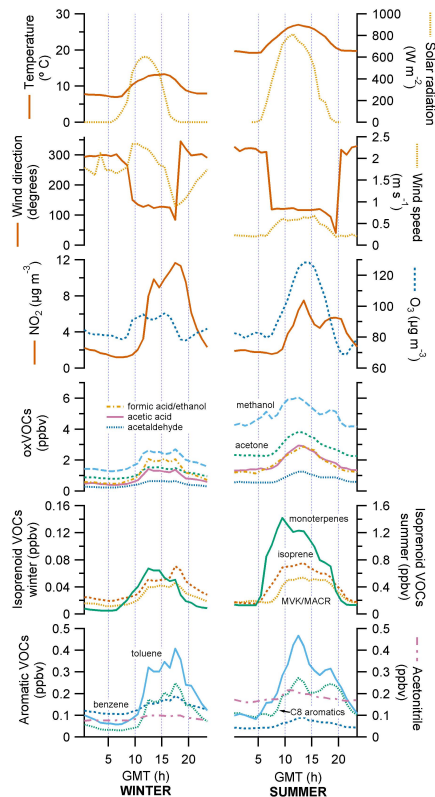


**Fig. 7.** Aromatic VOCs and acetonitrile showing their mixing ratios during the winter period (upper graph of each panel), their mixing ratios during the summer period (lower left graph) and their mean daily cycles (hourly averages) for both periods (lower right graph). Note the different scaling for the seasonal trend graphs. Date labels indicate 00:00 GMT.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## The effect of local biogenic emissions

R. Seco et al.



**Fig. 8.** Mean daily cycles of the majority of the variables studied, comparing winter (left) with summer (right). VOC mixing ratios are split into three separate panels, corresponding to Figs. 5, 6, and 7: (i) one for short-chain oxVOCs: methanol, acetone, formic acid/ethanol, acetic acid and acetaldehyde; (ii) the second one for isoprenoid VOCs: monoterpenes, and isoprene and its degradation products MVK/MACR; (iii) the last panel for acetonitrile and aromatic VOCs: benzene, toluene, and C8-aromatics. Note the different scaling for the isoprenoid VOCs between winter and summer (one order of magnitude higher in summer).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

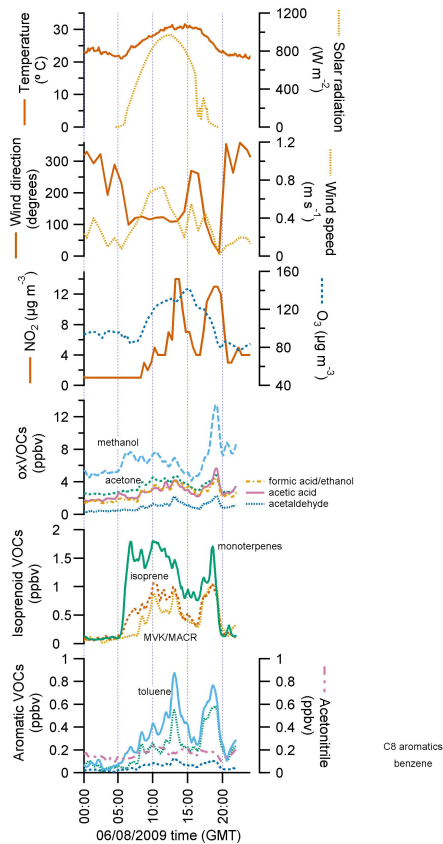
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Fig. 9.** Daily cycles of the majority of the variables studied, corresponding to the 6 August 2009. Panels and traces are the same as in Fig. 8.

**The effect of local biogenic emissions**

R. Seco et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

